

# When oil spills emulsify

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Understanding the factors that create stable water-in-oil emulsion will help in spill cleanup

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**C**leanup operations of oil spills must take into account the numerous detrimental effects attributable to the emulsification of spilled oil into a stable water-in-oil mousse. The incorporation of water greatly increases the volume of the polluted material. The viscous nature of mousse impedes the efficient operation of most mechanical recovery equipment and results in a cohesive slick that resists dispersion, both natural and artificial. The rate at which spilled oil emulsifies determines the effective window of opportunity for specific countermeasures.

Much has been learned from previous studies on petroleum emulsification (1-9), but it still remains a

poorly understood phenomenon. Although most crude oils can be emulsified, not all spills result in the formation of stable mousse. The formation of mousse results from a complex series of processes. Whether an oil will form mousse or not, and if so, at what rate, depends on an array of different factors including the properties of the oil and the prevailing environmental conditions. We need a greater understanding of the emulsification process to better predict the emulsification behavior of oil spills and utilize the most appropriate countermeasures available.

Here we report on work to elucidate the role that physicochemical factors play in determining an oil's tendency to emulsify. We studied the emulsification

behavior of oils of known composition to examine the importance of oil chemistry in the emulsification process.

It has long been recognized that indigenous petroleum emulsifying agents are concentrated in the higher boiling fractions (boiling point >370 °C) and particularly in the residuum (10). Asphaltenes, resins, and waxes are believed to be the main constituents of the interfacial films that encapsulate the water droplets contained in mousse (1, 2, 6). These films have high mechanical strength and thus act as effective physical barriers to prevent droplet coalescence (2, 5, 11–13). This in turn gives rise to the stable nature of mousse.

The main constituents of any oil can be grouped into four broad classes of compounds: alkanes, aromatics, resins, and asphaltenes. The lower molecular weight compounds in petroleum are generally alkanes and aromatics, whereas the resins, asphaltenes, and waxes account for the higher molecular weight compounds. Asphaltenes are the high molecular weight heterocycles that don't dissolve in CS<sub>2</sub>. Waxes are high molecular weight alkanes. In a complex mixture such as petroleum, all these compounds interact in such a way that all components are maintained in the liquid oil phase, i.e., the lighter components of the oil act as solvents for the higher molecular weight compounds. As long as this solvency interaction is maintained and thermodynamic conditions remain constant, the oil will remain stable. Should this equilibrium state be changed, a point will be reached where the solvency strength of the oil is insufficient to maintain the heavy components in solution and, as a result, they will precipitate out as solid particles. This is a frequent and problematic occurrence seen during petroleum production, transportation, and storage (14–17).

The precipitation of asphaltenes and waxes from oil has been modeled by several researchers (14–16) using the basic solubility theory as described by the Hildebrand–Scatchard equation (18). In this case, oil is viewed as being composed of a solute and a solvent. If one uses the solubility/precipitation behavior of asphaltenes, the solute consists of the asphaltenes and the solvent consists of the remaining compounds in the oil. The solubility behavior of asphaltenes in petroleum is:

$$RT \ln (A_a/X_a) = \frac{M_a \phi_s^2}{\rho_a} (\delta_a - \delta_s)^2$$

where:  $A_a$  = activity coefficient of asphaltenes  
 $X_a$  = mole fraction of asphaltenes  
 $M_a$  = molecular weight of asphaltenes  
 $\phi_s$  = volume fraction of solvent  
 $\delta_a$  = Hildebrand solubility parameter of the asphaltenes  
 $\delta_s$  = Hildebrand solubility parameter of the solvent  
 $\rho_a$  = density of asphaltenes  
 $R$  = gas constant  
 $T$  = temperature

With the assumption that asphaltenes are a homogeneous material and that  $A_a = 1$ , the above

equation can be rewritten in terms of the maximum amount of asphaltenes soluble in the oil,  $X_a$ .

$$\ln X_a = -\frac{M_a \phi_s^2}{\rho_a RT} (\delta_a - \delta_s)^2$$

If the amount of asphaltenes present in the oil exceeds  $X_a$ , the excess asphaltenes will precipitate.

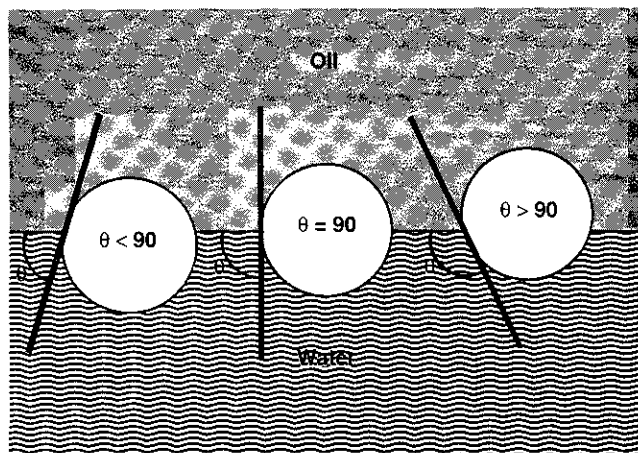
The role of solid particles in petroleum emulsification has been recognized for some time (19); however, the importance of this mechanism to mousse formation has not been completely appreciated. Examination of crude oil mousse using an electron microscope clearly showed particles in the interfacial film surrounding water droplets (4). Thompson and co-workers (9) showed that wax particles and associated solids exert considerable influence on the emulsion stability of a waxy North Sea crude. They found that removing the indigenous particles from this oil inhibited the oil's tendency to form stable emulsions. Similarly, Eley and co-workers (3) demonstrated that by varying the aromatic/aliphatic character of a synthetic oil containing asphaltenes, they could control the extent of emulsification.

For solids to act as emulsifying agents, the particles must be very small relative to the droplet size of the emulsified phase. They must collect at the interface and they must be "wetted" by both the oil and water phases. Figure 1 shows three ways that particles may distribute themselves between an oil–water interface. Water-in-oil emulsions form when the particle is preferentially wetted by the oil,  $\theta > 90^\circ$ . Oil-in-water emulsions form when the particle is preferentially wetted by water,  $\theta < 90^\circ$ . If the contact angle between the oil–water–solid boundary,  $\theta$ , deviates greatly from  $90^\circ$ , the emulsion will be unstable. Stable emulsions form when the contact angle is near  $90^\circ$  (2, 20).

To examine the nature of emulsification we prepared model oils consisting of an alkane component, an aromatic component, and the potential emulsifying agent(s).

#### Model oils

For experimental details in the preparation of model oils see references 21 and 22. Briefly we used asphaltenes, resins, and waxes as emulsifying agents, either individually or in combinations. Model oils were prepared by adding the emulsifying agent to the aromatic component. The mixture was vigorously shaken for 1 h. The alkane component was then added and the mixture was again shaken for 1 h. Then 30 mL of the oil was poured into a 500 mL flask containing 300 mL of artificial seawater and allowed to stand for approximately 20 h before being subjected to the emulsion formation and stability test (27). This test involves rotating the flask at 65 rpm for 1 h and then allowing the mixture to remain static for one-half hour before measuring the volume of the emulsion and the fraction of oil that emulsifies,  $F$ . The rotation/rest cycle is repeated three times. An indication of an oil's tendency to emulsify is given by  $F_0$ , the fraction of oil that emulsifies when  $F$  is extrapolated to time zero. The stability of the emulsion is obtained by allowing the emulsion to stand for 24 h and then measuring the fraction of oil that remains in the emulsion,  $F_{\text{final}}$ , as well as the water content of the stable emulsions.



**Figure 1.** Three ways solid particles may be distributed in an oil-water interface. The particle on the left is more wetted by the water than by the oil, thus being situated primarily in the aqueous phase, whereas the particle to the right exists primarily in the oil phase. The center situation illustrates a solid particle equally wetted by both the oil and water phase.

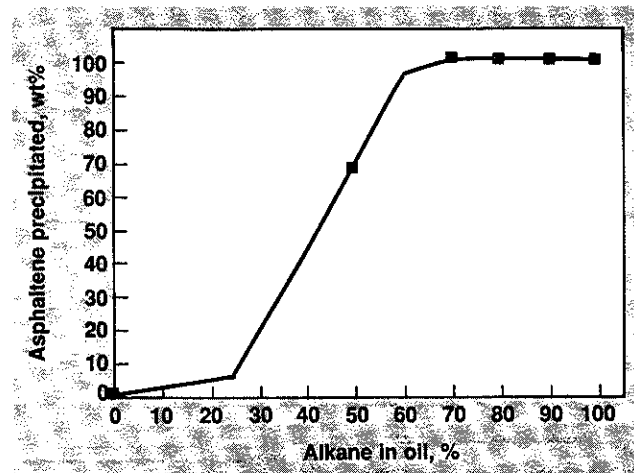
<b>Table 1. Emulsion behavior</b>	
$F_o$	Emulsion formation tendency
0 to 0.25	not likely
0.25 to 0.75	fairly likely
0.75 to 1	very likely
$F_{Final}$	Emulsion stability
0 to 0.25	unstable
0.25 to 0.75	fairly stable
0.75 to 1	very stable

$F_o$  = fraction of oil that emulsifies at  $t = 0$   
 $F_{Final}$  = fraction of oil that remains in emulsion after 24 hours

Mackay and Zagorski (7) classified emulsion behavior (Table 1).

### Asphaltenes as emulsifying agents

Figure 2 shows that the amount of asphaltenes precipitated out of the model oil depends on the alkane and aromatic composition of the oil. When these oils are subjected to the emulsification test, differences in the tendency to form stable emulsions are clearly evident (Figure 3). Figure 4 shows that there is a strong tendency ( $F_o = 1$ ) for this oil to emulsify when the alkane content is between 50 and 95% and these emulsions are stable ( $F_{Final} > 0.75$ ). Figure 5 shows that the emulsions have water contents between 50 and 90%. Yield point data that measure the force that must be applied to an emulsion to induce liquid flow show that a maximum yield point is



**Figure 2.** Percent of asphaltenes precipitated out of solution as a function of the alkane content of the oil.

Alkane component = heavy paraffin oil; aromatic component = xylene; asphaltene concentration = 0.05 g/mL.

reached when the model oil contains 80% alkane. Rheologically, this emulsion is the most stable for this series of model oils. It is at this point in the oil's composition that the asphaltene particles have the optimum size and contact angle with the interface to form emulsions. For the sake of comparison, two samples of mousse taken 18 days after the *Exxon Valdez* spill had yield points of 17 and 121 Pa under the same shear conditions.

We thus note that the alkane/aromatic ratio influences an oil's emulsification behavior and determines the amount of asphaltenes that will precipitate out of solution. Experiments using different concentrations of asphaltenes indicate that a minimum particulate concentration of about 0.03 g/mL must exist in the oil for stable emulsions to form. But it also appears that the alkane/aromatic ratio controls other factors involved in emulsification. The size of the asphaltene particles is determined by the alkane/aromatic ratio, particularly for the method by which we prepared these model oils. Asphaltenes were first dissolved in the appropriate quantity of xylene and then the paraffin oil was added; this causes the asphaltenes to precipitate out of solution. When the model oil is composed of 100% alkane, precipitation does not occur and the asphaltenes maintain their original aggregate size of approximately 1 micron. These particles are too large to effectively stabilize water droplets.

Figure 6 shows that the addition of asphaltenes to the alkane/aromatic mixtures lowers the interfacial tension between water and oil. However, an additional increase in

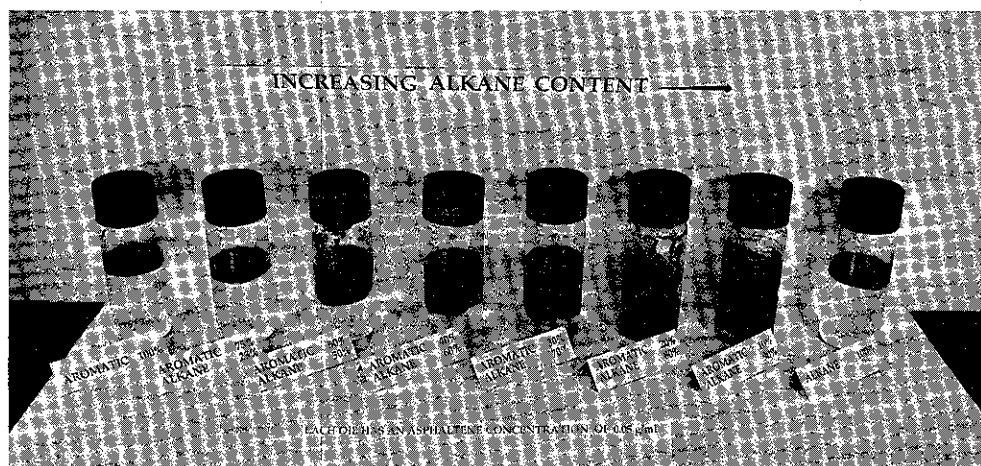


Figure 3. Appearance of model oils after undergoing the emulsion test.

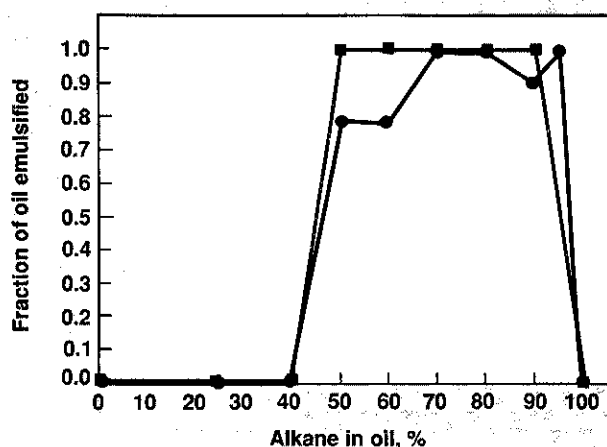


Figure 4. Emulsion formation tendency,  $F_o$  (■) and emulsion stability,  $F_{Final}$  (●) as a function of the alkane content of the oil.  $F_o = 0$  means there is no tendency to emulsify, and  $F_o = 1$  represents a strong tendency.  $F_{Final} = 0$  means emulsion completely broke after 24 h. All oil remains emulsified if  $F_{Final} = 1$ .

the concentration of asphaltenes has no apparent effect on the interfacial tension. This shows that when particulates are the emulsifying agent, extreme lowering of interfacial tension is not required to form emulsions, as is the case with typical surfactants (20).

#### Effect of changing alkane and aromatic components

From the Hildebrand-Scatchard equation, we see that the amount of asphaltenes soluble in oil,  $X_a$ , is controlled by the solubility parameters of the asphaltenes ( $\delta_a$ ) and the oil ( $\delta_s$ ). As  $(\delta_a - \delta_s)^2$  increases, the amount of asphaltenes soluble in oil decreases, and any excess

asphaltenes precipitate. Therefore, the probability of producing a stable emulsion should correlate with the value of  $(\delta_a - \delta_s)^2$ . When we plot  $F_{Final}$  values as a function of  $(\delta_a - \delta_s)^2$  we can see that stable emulsions only form when  $(\delta_a - \delta_s)^2$  has a value greater than or equal to approximately 60 MPa.

Solubility parameters can either be measured experimentally or calculated using compositional data. For the model oils, the solvency strength is determined by the alkane and aromatic composition. For aromatic compounds, the value of the solubility parameter decreases as the molecular weight is increased along a homologous series. Therefore, asphaltenes will be less soluble in model oils as the solubility parameter of the aromatic component is decreased. Our experiments showed that as the solubility parameter of the aromatic solvent decreased, the oil would form stable emulsions over a larger range of alkane/aromatic ratios.

The effect of using different alkane solvents as the precipitation medium for asphaltenes has been studied by Long and by Speight and Moschopedis (23, 24). Their findings indicate that as the chain length of the alkane solvent increases, the amount of asphaltenes that precipitate decreases, and that the composition of the precipitated material also changes. Higher alkane solvents yield asphaltenes with a higher degree of aromaticity, a higher proportion of heteroatoms, a higher degree of polarity, and higher molecular weights. Results from this study indicate that the model oils have a stronger tendency to form stable emulsions as the molecular weight of the alkane component increases, if the component is a mixture of alkanes (i.e., the paraffin oils) rather than a single alkane solvent.

To date, no study has examined either the change in solvency or the precipitation of asphaltenes as a function of oil weathering. But undoubtedly the rapid loss of  $C_{10}$



and lighter hydrocarbons from oil within hours of a spill (25) has a dramatic effect upon solvency and phase equilibrium. Results from our study indicate that the compositional changes that occur as a result of oil weathering would strongly favor the precipitation of asphaltenes and we speculate that spilled oil rapidly emulsifies into stable mousse once this precipitation is initiated. Weathered oil has a greater tendency to form mousse than does fresh oil, but this has largely been attributed to the physical changes induced by weathering. Indeed, weathering causes an increase in oil density and viscosity, and concentrates the indigenous emulsifiers in the remaining oil, also enhancing the formation of water-in-oil emulsions (20).

#### Resins and waxes as emulsifying agents

Figure 7 presents the emulsification behavior for model oils with various emulsifying agents. The results show that resins alone can act as effective emulsifiers. The range of alkane/aromatic ratios over which stable emulsions are produced is smaller than for asphaltene-containing oils. When asphaltenes and resins are both present, the range over which stable emulsions are formed is larger than either resins or asphaltenes alone.

Model oils containing only waxes as the emulsifying agent had no tendency to emulsify, but that behavior changes dramatically in the presence of asphaltenes. Figure 8 shows the effect of adding 0.05 and 0.1 g/mL of wax to a model oil containing 0.01 g/mL of asphaltenes. The oil containing 0.01 g/mL of asphaltenes had no tendency to form stable emulsions, but the addition of wax clearly increases such tendency at nearly all alkane/aromatic ratios. As the concentration of wax is increased, the oil has a greater tendency to produce stable emulsions.

Waxes are too hydrophobic to make enough contact with the interface to act as emulsifying agents by themselves. However, the waxes can interact with the asphaltenes in such a way that precipitated wax is able to stabilize the emulsion. It is estimated that when waxes constitute the majority of particles present in these oils, a minimum particulate concentration of around 0.06 g/mL must exist in the oil and that 0.01 g/mL of these particles must be asphaltenes.

#### Conclusions

Our study demonstrates the importance that the physical state of an emulsifying agent has upon its ability to stabilize emulsions. To be effective emulsifiers, asphaltenes, resins, and waxes must be in the form of finely divided submicron particles. The chemical composition of the oil determines not only the amount and size of these particles but also their composition and their wetting properties. All these factors influence the emulsification process.

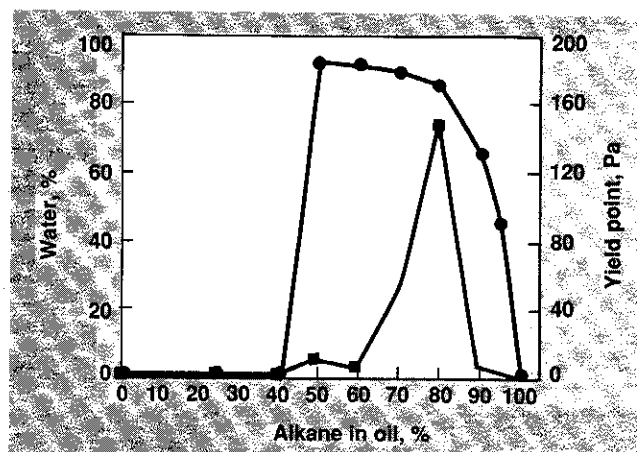


Figure 5. Water content (●) of stable emulsions formed, and yield point (■) of stable emulsions versus % alkane in oil. Programmed shear rate = 0 to 100 s<sup>-1</sup> in 10 min.

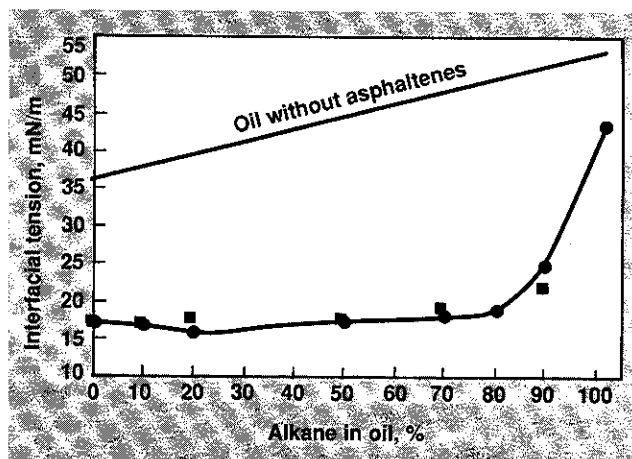


Figure 6. Effect of asphaltene concentration on oil-water interfacial tension. ■ = 0.025 g/mL asphaltenes; ● = 0.1 g/mL asphaltenes.

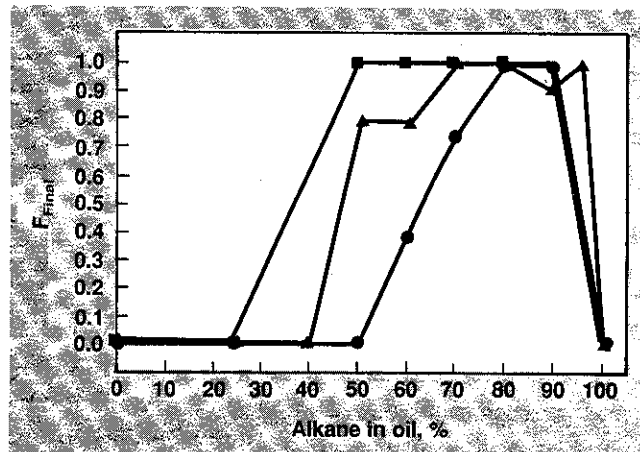
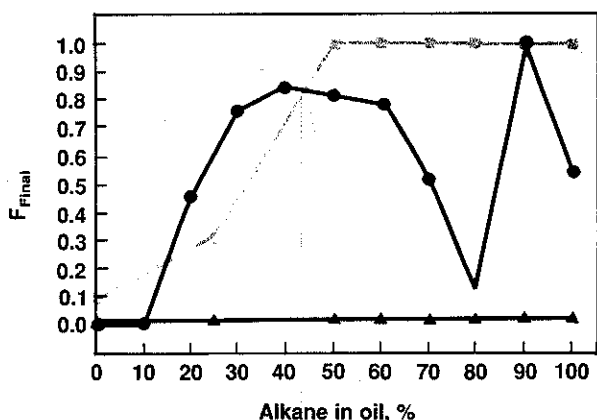


Figure 7. Comparison of  $F_{Final}$  for oils containing resins and asphaltenes, individually and in combination.

▲ = 0.05 g/mL asphaltenes; ● = 0.5 g/mL resins; ■ = 0.05 g/mL asphaltenes + resins.

Asphaltenes and resins, by themselves and in combination, were effective emulsifying agents. Model oils containing only wax as the emulsifying agent did not form stable emulsions. But the addition of a nominal amount of asphaltenes, an amount insufficient by itself to



**Figure 8. Effect of adding wax to an asphaltene-containing model oil.** ▲ = 0.01 g/mL asphaltenes + 0 wax; ● = 0.01 g/mL asphaltenes + 0.05 g/mL wax; ■ = 0.01 g/mL asphaltenes + 0.1 g/mL wax.

produce emulsions, to oils containing wax led to the formation of stable emulsions. This indicates that different emulsifying particulates can synergistically interact to stabilize emulsions.

The solubility/precipitation behavior of asphaltenes in model oils follows the solubility theory as described by the Hildebrand-Scatchard equation. Therefore, it could potentially be adapted to model the precipitation behavior of indigenous petroleum emulsifiers as spilled oil weathers, and thus be used to predict the physicochemical conditions in oil that favor mousse formation.

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### References

- (1) Bridie, A. L.; Wanders, T.H.H.; Zegveld, W.; Vander Heijde, H. B. *Marine Pollution Bull.* **1980**, *11*, 343.
- (2) Canevari, G. P. *Marine Pollution Bull.* **1982**, *13*(2), 49.
- (3) Eley, D. D.; Hey, M. J.; Symonds, J. D. *Colloids Surf.* **1988**, *32*, 87.
- (4) Eley, D. D.; Hey, M. J.; Symonds, J. D.; Willison, J.H.M. *J. Colloid Interface Sci.* **1976**, *54*, 462.
- (5) Jones, T. J.; Neustadter, E. L.; Whittingham, K. P. *J. Can. Pet. Technol.* **1978**, *17*(2), 100.
- (6) Mackay, D. *Formation and Stability of Water-in-oil Emulsions*; Environment Canada Report EE-93, 1987.
- (7) Mackay, D.; Zagorski, W. *Studies of Water-in-oil Emulsions*; Environment Canada Report EE-34, 1982.
- (8) Mackay, G.C.M.; McLean, A. Y.; Betancourt, O. J.; Johnson, B. C. *J. Inst. Pet.* **1973**, *5*, 164.
- (9) Thompson, D. G.; Taylor, A. S.; Graham, D. E. *Colloids Surf.* **1985**, *15*, 175.
- (10) Lawrence, A.S.C.; Killner, W. *J. Inst. Pet.* **1948**, *34*(299), 821.
- (11) Eley, D. D.; Hey, M. J.; Lee, M. A. *Colloids Surf.* **1987**, *24*, 173.
- (12) Blair, C. M. *Chem. Ind.* **1960**, 538.
- (13) Hasiba, H. H.; Jessen, F. W. Film Forming Compounds from Crude Oils, Interfacial Films and Paraffin Deposition. *Proceedings of 18th Annual Technical Meeting Petroleum Society*, 1967. *J. Can. Pet. Technol.*, Jan.-Mar. 1968, p. 1.
- (14) Griffith, M. G.; Siegmund, C. W. In *Marine Fuels*; Jones, C. H., Ed.; ASTM STP 878, American Society for Testing and Materials: Philadelphia, 1985, p. 227.
- (15) Kawanaka, S.; Leontaritis, K. J.; Park, S. J.; Mansoori, G. A. In *Enhanced Recovery and Production Stimulation*; Borchardt, J. K.; Yen, T. F., Eds. American Chemical Society: Washington, D.C., 1989; Ch. 24, p. 443.
- (16) Majeed, A.; Bringedal, B.; Overa, S. *Oil Gas J.* June 18, 1990; p. 63.
- (17) Mochida, I.; Sakanishi, K.; Fujitsu, H. *Oil Gas J.* Nov. 17, 1986.
- (18) Barton, A.F.M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, Fla., 1983.
- (19) Van der Waarden, M. *Kolloid Z.* **1958**, *156*, 116.

- (20) Becher, P. *Encyclopedia of Emulsion Technology*; Marcel Dekker: New York, 1983; p. 1.
- (21) Bobra, M. *A Catalogue of Crude Oil and Oil Product Properties*; Environment Canada Report EE-114, 1989.
- (22) Bobra, M. A Study of the Formation of Water-in-Oil Emulsions. *Proceedings of 1990 Arctic and Marine Oilspill Program Technical Seminar*, Edmonton, Alberta. Ministry of Supply and Services Canada, Cat. No. EN 40-11/5-1990; p. 87.
- (23) Long, R. B. In *Division of Petroleum Chemistry Symposium*; American Chemical Society: Washington, D.C., 1979; p. 891.
- (24) Speight, J. G.; Moschopedis, S. E. In *Division of Petroleum Chemistry Symposium*; American Chemical Society: Washington, D.C., 1979; p. 90.
- (25) McAuliffe, C. D. In *Proceedings of the 1989 Oil Spill Conference*; San Antonio, p. 357. American Petroleum Institute: Washington, D.C.; Publication No. 4479.

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